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Molecular tectonics: control of pore size and polarity in 3-D hexagonal coordination networks based on porphyrins and a zinc cation†

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Received (in Cambridge, UK) 25th July 2008, Accepted 9th September 2008
First published as an Advance Article on the web 24th September 2008
DOI: 10.1039/b812831f

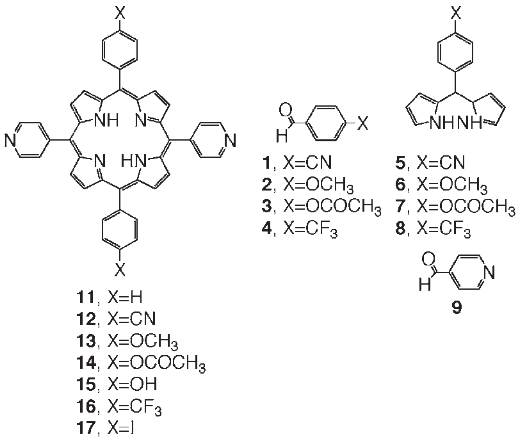
In the crystalline phase, porphyrin derivatives based on two 4-pyridyl units at the 5 and 15 *meso* positions and two 4-aryl moieties bearing various groups (CN, OMe, OH and $\mathrm{CF_3}$) at the 10 and 20 *meso* positions lead, in the presence of a zinc dication, to the formation of robust 3-D networks presenting hexagonal channels: both the size and the polarity of the pores were tuned by the nature of the substituents attached to the two aryl groups.

Porous crystalline coordination networks[1] are interesting solid materials offering a variety of properties such as gas storage and catalysis. This type of infinite architecture may be conceived by the molecular tectonics approach[2] based on the combination of organic and metallic tectons[3] capable of mutual interconnection. In order to encapsulate guest molecules, the control of pore size and polarity remains one of the numerous challenges in this area. Among various organic tectons leading to the formation of coordination networks, porphyrin derivatives bearing additional coordination sites at their periphery are particularly interesting units.[4] We[5] and others[6] have reported several examples of coordination networks based on a variety of porphyrin derivatives.

Here, we report on the control of pore size and polarity achieved by combining porphyrin based tectons **12–16** bearing two 4-pyridyl and two functionalised 4-aryl units with a Zn^{2+} cation.

In the course of our previous study using a combination of the porphyrin **11** (Scheme 1) and Zn^{2+} cation, we have described the formation of a 3-D hexagonal type coordination network possessing channels occupied by solvent molecules (Fig. 1).[7]

The same type of arrangement has been also reported for the tetrapyridyl analogue of **11**[6g,i] and for tecton **17**.[6h] The crystalline material obtained with **11** appeared to be particularly stable and the exchange of solvent molecules could be performed reversibly without loss of structural integrity of the crystal (single-crystal-to-single-crystal transformation). Based on this observation, we thought that this type of architecture was an ideal case for demonstrating the control of both pore size and polarity. Thus, the analogues **12–16** were designed and prepared. All these compounds bear two 4-pyridyl units at the 5 and 15 *meso* positions behaving as secondary coordination sites and thus participating in the formation of the network through coordination with the Zn^{2+} cation located within the centre of the porphyrin ring (primary coordination site) and two 4-aryl groups bearing various groups (CN, OMe, OH and $\mathrm{CF_3}$) at the 10 and 20 *meso* positions. Based on the design principle depicted in Fig. 1, the latter groups should be oriented within the channels, and thus should allow us to control both the size and the polarity of pores.



Scheme 1

The synthesis of compounds **12–16** was achieved in 6–11% yield using the slightly modified (mainly time of reaction) procedure reported by Gryko[8] by condensing the pyridyl carboxaldehyde **9** with the dipyrromethane derivatives **5–8** in $\mathrm{CH_2Cl_2}$ in the presence of trifluoroacetic acid. Compounds **5**,[9a] **6**[9b] and **8**[9c] were prepared in 76–89% yield upon reaction of aldehydes **1**, **2** and **4** with pyrrole in the presence of $\mathrm{BF_3{\cdot}Et_2O}$. Compounds **12**[10] and **13**[9b] have been previously reported. However, to the best of our knowledge, the synthesis of compounds **7**, **14** and **16** have not been documented in the literature (for synthesis and characterisation of all three compounds, see ESI†). Both final compounds **14** and **16** were characterised by classical methods as well as by X-ray diffraction on single crystals (see ESI†).‡ The compound **15**, previously reported,[9b] was obtained *in situ* in the crystallisation tube by hydrolysis of the compound **14**.

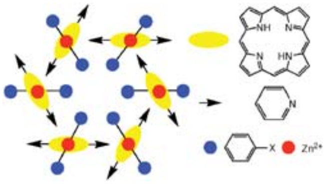


Fig. 1 Schematic representation of a portion of the projection in the plane perpendicular to the *c* axis showing the control and polarity of channels. Solvent molecules are omitted for clarity.

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† Electronic supplementary information (ESI) available: Experimental. CCDC reference numbers 696294–696299, 701453. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b812831f

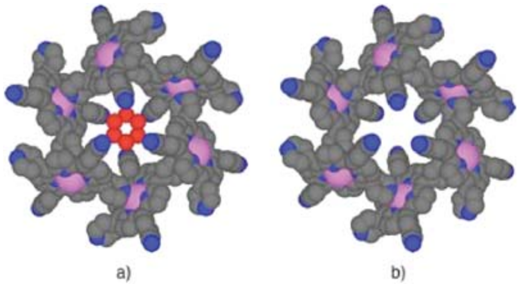

Fig. 2 Portions of structures of hydrated (a) and dehydrated (b) hexagonal 3-D networks formed upon combining the tecton **12** bearing two nitrile groups with a Zn^{2+} cation. H atoms are not presented for clarity.

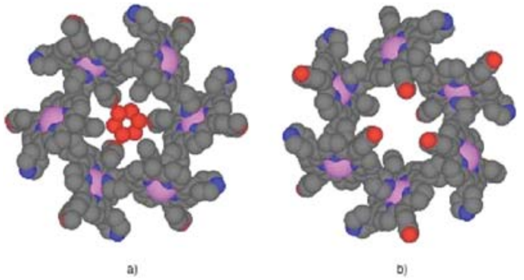

Fig. 3 Portions of structures of hexagonal 3-D networks formed upon combining the tecton **13** bearing two OMe groups (a) and the tecton **15** bearing two OH groups (b) with a Zn(II) cation. In the case of **15** solvent molecules could not be refined. H atoms are not presented for clarity.

For all tectons **12** (Fig. 2a), **13** (Fig. 3a) and **15** (Fig. 3b), upon slow diffusion of a $CHCl_3$ solution (0.5 mL) of the porphyrin derivative (0.5 mg) into a MeOH (0.5 mL) of $Zn(OAc)_2{\cdot}2H_2O$ (40 eq.), single crystals suitable for X-ray diffraction were obtained after several days. In all three cases, as in the case of **11** previously reported,[7] the structural analysis revealed isostructural hexagonal type 3-D networks (*Rhombohedral*, space group $R\bar{3}$).§ The Zn^{2+} cation adopts a deformed octahedral geometry with its coordination sphere composed of 6 N atoms, 4 belonging to the porpyrin core (Zn–N distance in the range of 2.057(7) and 2.072(2) Å) and two to pyridine units belonging to two consecutive tectons (Zn–N distance in the range of 2.317(11) and 2.357(3) Å). The tilt between the mean plane (24 atoms) of consecutive porphyrins is in the range of 81.87° and 83.10°. The tilt angle between the axial pyridine units and the plane of the porphyrin is in the range of 68.12° and 69.41°. For both networks obtained using tectons **12** and **13**, the channels are filled with H-bonded ($d_{O\text{–}O}$ of *ca.* 2.82 Å) H_2O molecules (2 H_2O per tecton **12**, 2 disordered (multiplicity of 0.5) H_2O per tecton **13**). No H-bonding interactions between the water molecules and the CN ($d_{O\text{–}N}$ = 3.24 Å) or MeO ($d_{O\text{–}O}$ = 5.01 Å) groups are present in the structure. In the case of **15**, the solvent molecules could not be refined.

The robustness of the architecture was established in the case of the 3-D network obtained with both tecton **12** and **13** (not reported). Indeed, for **12**, the crystal was heated under vacuum to 100 °C for 24 h. The material remained crystalline and the study by X-ray diffraction on single crystal revealed the structural integrity of the 3-D framework (Fig. 2 right). Upon removal of solvent molecules the unit cell parameters are only slightly changed (dehydrated: $a = b = 32.985$ Å, $c = 9.038$ Å and $V = 8516.7$ Å^3, hydrated: $a = b = 32.934$ Å, $c = 9.164$ Å and $V = 8608.3$ Å^3). The same type of reversible single-crystal-to-single-crystal transformation was also reported for the tecton **11**.[7]

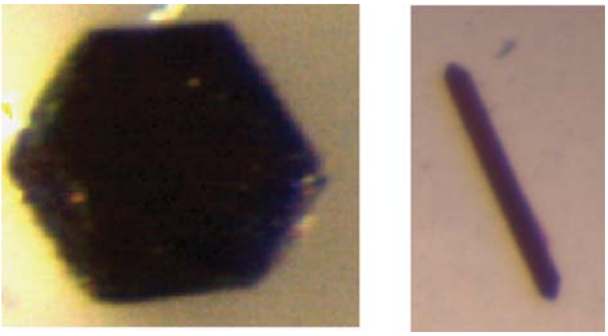

Fig. 4 Photographs of 3-D (hexagonal, left) and 1-D (rod, right) crystals obtained upon combining tecton **16** bearing two CF_3 groups with a Zn^{2+} cation.

In the case of tecton **16**, upon slow diffusion of a $CHCl_3$ solution (0.5 mL) of the porphyrin derivative **16** (0.5 mg) into a MeOH solution (0.5 mL) of $Zn(OAc)_2{\cdot}2H_2O$ (40 eq.), two types of crystals (hexagonal, α phase and rod, β phase) were obtained after several days (Fig. 4).§ Interestingly, under precisely the same conditions, the cystallisation process leads either to the formation of hexagonal or rod type morphologies. A mixture of both shapes within the same crystallisation tube was never observed. The X-ray diffraction on hexagonal crystals (*rhombohedral*, space group $R\bar{3}$) revealed that the latter corresponds to the same type of 3-D architecture (Fig. 5a) as the one obtained for tectons **11–13** and **15**. Indeed, the Zn^{2+} cation adopts a deformed octahedral geometry with its coordination sphere composed of 4 N atoms belonging to the porpyrin core ($d_{Zn\text{–}N}$ = 2.056(3) and 2.064(3) Å) and two pyridyl units belonging to two consecutive tectons **16** ($d_{Zn\text{–}N}$ 2.357(3) Å). The mean plane (24 atoms) of consecutive porpyrins are tilted by 82.83°. The axial pyridine units are not perpendicular to the plane of the porphyrin but tilted by 68.12°. The channels are filled with H-bonded ($d_{O\text{–}O}$ of *ca.* 2.95 Å) H_2O molecules (2 molecules per tecton **16**).

For the rod type crystals, the structural analysis revealed the formation of a 1-D network (Fig. 5b). Indeed, in that case, the Zn^{2+} cation is pentacoordinated and its coordination sphere (square based pyramidal geometry) is composed of 4 N atoms belonging to the porphyrin core ($d_{Zn\text{–}N}$ in the range of 2.052(6) and 2.079(6) Å) and one pyridine belonging to the neighbour tecton **16** ($d_{Zn\text{–}N}$ 2.134(6) Å). The mean plane (24 atoms) of

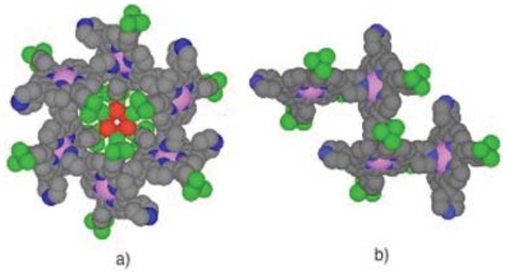

Fig. 5 Portions of the structures of hexagonal 3-D (a) and 1-D (b) networks formed upon combining the tecton **16** bearing two CF_3 groups with a Zn(II) cation. H atoms are not presented for clarity.

consecutive porphyrins are tilted by 86.01°. The axial pyridine is tilted by 75.91° with respect to the mean plane of the porphyrin. The porphyrin unit is slightly ruffled and the Zn^{2+} cation is out of the porphyrin mean plane by 0.384 Å. The crystal contains $CHCl_3$ solvent molecules without any specific interactions with the framework.

The comparison of voids ($Å^3$, calculated by platon software, solvent molecules virtually removed) of all four 3-D networks obtained here using tectons **12** (277), **13** (250), **15** (463) and **16** (295) with those calculated for the reported isostructural networks generated using tectons **11** (585)[7] and **17** (302)[6h] clearly demonstrated the possibility of modulating the size of the hexagonal channels.

In conclusion, the combination of porphyrins bearing two 4-pyridyl units as secondary coordination sites and two 4-aryl units bearing various functionalities (CN, OMe, OH and CF_3) as decorating groups at the 5,15 and 10,20 *meso* positions, respectively, and Zn^{2+} leads to the formation of isostructural robust hexagonal 3-D networks. We have demonstrated that, in the crystalline phase, both the size and polarity of channels may be controlled by the proper choice of porphyrin derivatives.

Extension to other porphyrin derivatives and metal cations as well as the study of solvent and gas molecules uptake are currently under way.

We thank the Université Louis Pasteur, the Institut Universitaire de France, the Ministry of Education and Research, the CNRS and Marie Curie EST Actions FUMASSEC Network (Contrat N° MEST-CT-2005-020992) for financial support.

Notes and references

‡ Crystallography: data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97.[11] The hydrogen atoms were introduced at calculated positions and not refined (riding model). H atoms of water molecules were not determined.

§ Crystal data for dehydrated **12**-Zn: $C_{44}H_{24}N_8Zn$, M = 730.08, *trigonal*, space group $R\bar{3}$, $a = b$ = 32.9851(7), c = 9.0387(4) Å, $\alpha = \beta$ = 90°, γ = 120°, V = 8516.7(5) $Å^3$, T = 173(2) K, Z = 9, D_c = 1.281 g cm^{-3}, μ = 0.691 mm^{-1}, 26 849 collected reflections, 4342 independent (R_{int} = 0.0851), GooF = 1.074, R_1 = 0.0609, wR_2 = 0.1450 for $I > 2\sigma(I)$ and R_1 = 0.1079, wR_2 = 0.1722 for all data.

Crystal data for hydrated **12**-Zn·$2H_2O$: $C_{44}H_{28}N_8O_2Zn$, M = 766.11, *trigonal*, space group $R\bar{3}$, $a = b$ = 32.9346(7), c = 9.1639(4) Å, $\alpha = \beta$ = 90°, γ = 120°, V = 8608.3(5) $Å^3$, T = 173(2) K, Z = 9, D_c = 1.323 g cm^{-3}, μ = 0.690 mm^{-1}, 34 324 collected reflections, 4393 independent (R_{int} = 0.0564), GooF = 1.052, R_1 = 0.0623, wR_2 = 0.1624 for $I > 2\sigma(I)$ and R_1 = 0.0829, wR_2 = 0.1781 for all data.

Crystal data for **13**-Zn: $C_{44}H_{32}N_6O_3Zn$, M = 758.13, *trigonal*, space group $R\bar{3}$, $a = b$ = 32.8450(3), c = 9.2054(2) Å, $\alpha = \beta$ = 90°, γ = 120°, V = 8600.3(2) $Å^3$, T = 173(2) K, Z = 9, D_c = 1.314 g.cm^{-3}, μ = 0.691 mm^{-1}, 30 620 collected reflections, 4384 independent (R_{int} = 0.0655), GooF = 1.034, R_1 = 0.0572, wR_2 = 0.1584 for $I > 2\sigma(I)$ and R_1 = 0.0717, wR_2 = 0.1719 for all data.

Crystal data for **15**-Zn, $C_{42}H_{26}N_6O_2Zn$, M = 712.06, *trigonal*, space group $R\bar{3}$, $a = b$ = 32.941(2), c = 9.4384(11) Å, $\alpha = \beta$ = 90°, γ = 120°, V = 8869.5(13) $Å^3$, T = 173(2) K, Z = 9, D_c = 1.200 g cm^{-3}, μ = 0.664 mm^{-1}, 4521 collected reflections, 4521 independent (R_{int} = 0.22), GooF = 0.22, R_1 = 0.1057, wR_2 = 0.2487 for $I > 2\sigma(I)$ and R_1 = 0.2053, wR_2 = 0.2888 for all data. Water molecules could not be refined and thus the squeeze command was used.

Crystal data for **16**-Zn α phase: $C_{44}H_{28}F_6N_6O_2Zn$, M = 852.09, *trigonal*, space group $R\bar{3}$, $a = b$ = 33.1347(4), c = 9.1686(3) Å, $\alpha = \beta$ = 90°, γ = 120°, V = 8717.7(3) $Å^3$, T = 173(2) K, Z = 1, D_c = 1.461 g cm^{-3}, μ = 0.710 mm^{-1}, 26 919 collected reflections, 4513 independent (R_{int} = 0.0738), GooF = 1.202, R_1 = 0.0628, wR_2 = 0.1780 for $I > 2\sigma(I)$ and R_1 = 0.1160, wR_2 = 0.2028 for all data.

Crystal data for **16**-Zn β phase: $C_{45}H_{25}Cl_3F_6N_6Zn$, M = 935.43, *monoclinic*, space group $P2_1/n$, a = 17.0482(11), b = 14.1382(10), c = 17.2892(11) Å, $\alpha = \gamma$ = 90°, β = 101.433(3)°, V = 4084.5(5) $Å^3$, T = 173(2) K, Z = 4, D_c = 1.521 g cm^{-3}, μ = 0.867 mm^{-1}, 22 805 collected reflections, 9223 independent (R_{int} = 0.0881), GooF = 1.162, R_1 = 0.0976, wR_2 = 0.2227 for $I > 2\sigma(I)$ and R_1 = 0.2317, wR_2 = 0.2781 for all data.

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